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Treatment Technology for Pesticide Manufacturing Effluents: Bentazon

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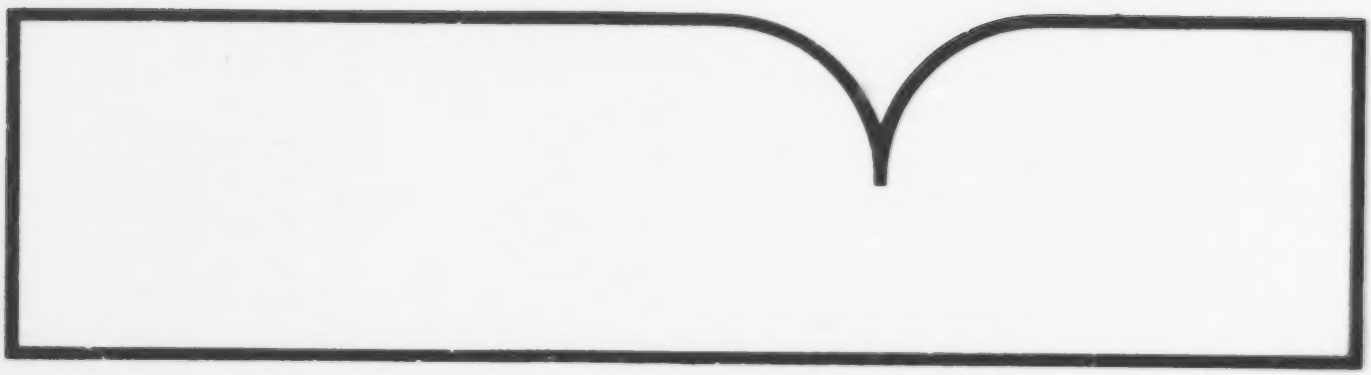

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TREATMENT TECHNOLOGY FOR PESTICIDE MANUFACTURING EFFLUENTS: BENTAZON

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16. ABSTRACT The report gives results of laboratory studies of the treatability of wastewater generated from the manufacture of bentazon. The wastewater was characterized for pesticide content by high performance liquid chromatography (HPLC). Toxicity determinations on bentazon and its major treatment product (dichlorobentazon) were conducted with Daphnia Magna. Bentazon was not toxic to the daphnids at concentrations of up to 50 ppm. The major known by-product of chlorination of bentazon is dichlorobentazon, which is toxic to daphnids at 50 ppm. The removal of bentazon from wastewater by treatment with sodium hypochlorite was emphasized. The effects of variations in the pH, amount of hypochlorite, temperature, and mode of hypochlorite addition were studied. Temperature and the mode of addition had little effect on the removal of bentazon. It was found that bentazon is most efficiently removed by hypochlorite when the pH is 2 or below and when a 245- to 370-fold excess of hypochlorite is used. Based on assumed rates of process wastewater production, the total cost of the treatment was estimated.

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ABSTRACT

Laboratory studies were conducted on the treatability of wastewater generated from the manufacture of bentazon. The wastewater was characterized for pesticide content by high performance liquid chromatography. Toxicity determinations on bentazon and its major treatment product, dichlorobentazon, were conducted with Daphnia Magna. Bentazon was not toxic to the daphnids at concentrations of up to 50 ppm. The major by-product of chlorination of bentazon is dichlorobentazon which is toxic to daphnids at 50 ppm.

Emphasis was placed on the removal of bentazon from wastewater by treatment with sodium hypochlorite. The effects of variations in the pH, amount of hypochlorite, temperature, and mode of hypochlorite addition were studied. The temperature and mode of addition had little effect on the removal of bentazon. It was found that bentazon was most efficiently removed by hypochlorite when the pH was 2 or below and when a 245- to 370-fold excess of hypochlorite was used.

Based on assumed rates of process wastewater production, the total cost of the treatment was estimated.

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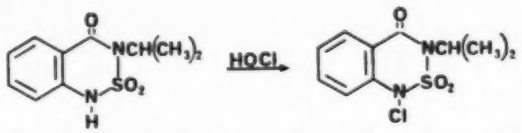
SECTION 1

INTRODUCTION

This report describes a study of the treatability of wastewater resulting from the manufacture of bentazon. The objective of this project was to conduct a bench-scale treatability study of bentazon pesticide manufacturing wastewater using treatment with sodium hypochlorite. Pesticide removal was the principal criterion for evaluating the usefulness of each control treatment. Wastewater treatment operating conditions were chosen to simulate actual commercial units in such parameters as contact time, temperature, etc., so that meaningful treatment cost estimates for manufacturing processes could be generated.

Under proposed Effluent Guidelines for Pesticides, bentazon may be regulated as part of Category 2 pesticides. Based on production, the allowable discharge per day is therefore four pounds, or a concentration of 2.5 ppm with a flow of 135 gpm leaving the carbon unit. Preliminary studies conducted by BASF Wyandotte have shown that oxidation with sodium hypochlorite is effective in destroying bentazon in the wastewater. Hypochlorite reacts with bentazon as shown below.



Excess hypochlorite is destroyed with sodium bisulfite before the wastestream reaches the biotreatment facility.

The large excess of hypochlorite increases the salt content of the wastewater, and free chlorine and bisulfite can also be pollutants. Other organic materials may react with hypochlorite to form products which may be harmful.

The treatment costs were based upon the results of the test program, that is, the equivalents of hypochlorite required for bentazon removal, residence time, amount of bisulfite required to destroy excess hypochlorite.

While the goal of the treatment is to reduce bentazon to the 4 lbs/day level, consideration must be given to the problems of the generation of additional pollutants and requirements for compatability with a downstream biotreatment plant.

SECTION 2

RESULTS AND CONCLUSIONS

The following results were obtained from this hypochlorite treatment study of bentazon-containing wastewater.

(1) The analytical HPLC method was used successfully to monitor bentazon levels in wastewater samples.

(2) Assuming a stoichiometry of 2 equivalents hypochlorite to 1 equivalent bentazon, the excess hypochlorite (5% aqueous sodium hypochlorite) required for complete bentazon removal was between 245 and 370-fold.

(3) Bentazon disappeared rapidly as long as the wastewater pH was 2 or below with the use of a 333-fold excess of hypochlorite. A higher initial pH resulted in incomplete bentazon removal.

(4) The effect of temperature on the reaction was of secondary importance over the temperature range which the wastewater would encounter. Water temperatures between 3°-7°C may slow the reaction a little (the smaller the excess of hypochlorite, the greater the slowing effect), but with a 333-fold excess the effect was very small.

(5) The mode of addition of hypochlorite had no effect on the treatment process. As long as the correct excess was added, whether all at once or in portions, the final result was the same.

(6) Dichlorobentazon was the major product of the reaction of bentazon with excess hypochlorite in acidic solutions. Other product(s) have not been identified.

(7) Bentazon was essentially nontoxic to Daphnia Magna up to at least 50 ppm. The major treatment product of bentazon, dichlorobentazon, was toxic to Daphnia Magna at 50 ppm, with some toxicity also at 5 ppm and 0.5 ppm.

(8) The estimated unit cost of hypochlorite treatment was $0.0714 per gallon. Annualized costs were estimated at approximately 3.6 million dollars/year.

SECTION 3

RECOMMENDATIONS

The experimental findings have lead to the following suggestions for future work.

(1) Other treatment approaches should be attempted to develop a system with a product less toxic than bentazon or upgrade current treatment to produce less bentazon in wastewater.

(2) Treatment conditions should be investigated in an effort to reduce the hypochlorite excess required for complete bentazon removal (e.g., catalysis, nature of the acidic agent).

SECTION 4

SELECTED LITERATURE REVIEW

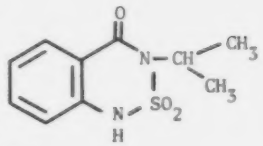
PESTICIDE

Bentazon CAS No. 25057-89-0

NAMES

Bentazone
Basagran

STRUCTURE



$C_{10}H_{12}N_2O_3S$

Mol. Wt. 240.3

CHEMICAL NAMES

3-Isopropyl-1H-benzo-2,1,3-thiadiazin-4-one-2,2-dioxide; 3-Isopropyl-1H-2,1,3-benzothiadiazion-(4)-3H-one 2,2-dioxide; 1H-2,1,3-Benzothiadiazin-4(3H)-one, 3-(1-methylethyl) 2,2-dioxide.

CHEMICAL CATEGORY

Benzothiadiazine

PROPERTIES

Bentazon is a white solid that is 200 ppm soluble in water below pH 2 and 47% above pH 9 (BASF Wyandotte). Bentazon is weakly acidic (pK_a = 3.2).

INTENDED USES

Bentazon is a postemergence herbicide used to control broadleaf weeds in most grains and many large-seeded leguminons crops (Weed Society).

The following tolerances set by EPA for Bentazon in or on raw agricultural commodities have been listed by Sittig (1980):

	CFR Reference	per Million
Beans (exc. soybeans), dry	180.355	0.05
Beans (exc. soybeans), vinehay	180.355	3.0
Beans, lima	180.355	0.05
Beans, succulent	180.355	0.5

Cattle, fat	180.355	0.05
Cattle, mbyp	180.355	0.05
Cattle, meat	180.355	0.05
Corn, fodder	180.355	3.0
Corn, forage	180.355	3.0
Corn, fresh (inc. sweet)(k = cwhr)	180.355	0.05
Corn, grain	180.355	0.05
Eggs	180.355	0.05
Goats, fat	180.355	0.05
Goats, mbyp	180.355	0.05
Goats, meat	180.355	0.05
Hogs, fat	180.355	0.05
Hogs, mbyp	180.355	0.05
Hogs, meat	180.355	0.05
Horses, fat	180.355	0.05
Horses, mbyp	180.355	0.05
Horses, meat	180.355	0.05
Milk	180.355	0.02
Mint	180.355	1.0
Peanuts	180.355	0.05
Peanuts, hay	180.355	3.0
Peanuts, hulls	180.355	0.3
Peas, dry	180.355	0.05
peas, dry, vinehay	180.355	3.0
Peas, succulent	180.355	0.5
Poultry, fat	180.355	0.05
Poultry, mbyp	180.355	0.05
Poultry, meat	180.355	0.05
Rice	180.355	0.05
Rice, straw	180.355	3.0
Sheep, fat	180.355	0.05
Sheep, mbyp	180.355	0.05
Sheep, meat	180.355	0.05
Soybeans	180.355	0.05
Soybeans, hay	180.355	0.3

The tolerances set by EPA for Bentazon in animal feeds have been listed by Sittig (1980):

Mint hay	561.51	4.0

MANUFACTURING INFORMATION

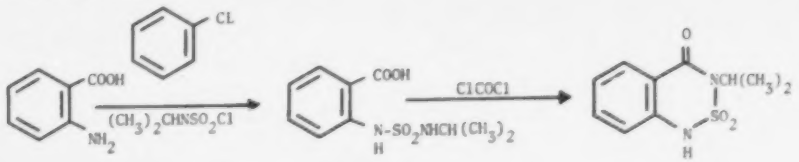
The sole manufacturer of Bentazon in the USA is BASF Wyandotte of Geismar, LA. Bentazon was introduced in 1976.

ANNUAL PRODUCTION

Annual production data is not available.

MANUFACTURING PROCESS

Bentazon is made by the reaction of anthranilic acid with isopropylsulfamoyl chloride in the presence of chlorobenzene to give N-(isopropylsulfamoyl)-anthranilic acid which is then cyclized in the presence of phosgene to give bentazon (Sittig, 1980).



HEALTH EFFECTS AND ECOLOGICAL EFFECTS

Toxocity

Preliminary toxicity studies have provided the following information:

LD_{50} = 1,100 mg/kg, male rat (oral)
= 900 mg/kg, dog
= 720 mg/kg, quail
= 500 mg/kg, cat

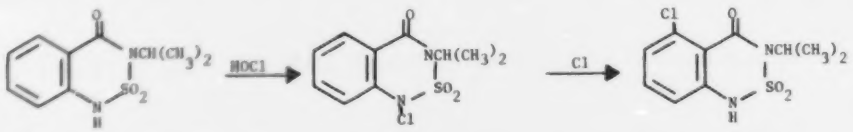
The male rat datum was taken from "Analytical Standards and Supplemental Data for Pesticide and other Organic Compounds", J. F. Thompson and R. R. Watts, EPA-600/9-78-012, HERL, EPA, RTP, NC, May 1978. Other toxicity values were obtained from BASF Wyandotte.[3]

DEGRADATION

Very little information is available on the degradation of bentazon. Preliminary studies conducted by BASF Wyandotte have shown that oxidation with sodium hypochlorite was effective in destroying bentazon in the wastewater. Hypochlorite reacts with bentazon as shown below. The positive chlorine atom is probably the active species in this reaction.

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$
$$HCl + HOCl \xrightarrow{NaOH} NaCl + HOCl\ (NaOCl)$$
$$HOCl \longrightarrow HO^- + Cl^+$$
$$NaOCl \longrightarrow Na^+ + OCl \xrightarrow{-H_2O} NaOH + OH^- + Cl^+$$

BASF Wyandotte also suggested that the N-chloro compound may rearrange via the Orton Rearrangement to chlorinate the benzene ring.



An alternative treatment to chlorination involves the addition of peroxide to the bentazon stream. This approach was found by the manufacturer to be inadequate.

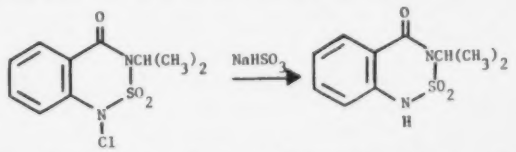
SECTION 5

TREATABILITY STUDIES

Samples of bentazon manufacturing wastewater were obtained from the manufacturer. Figure 1 is a diagram of the plant treatment system with sampling points indicated. Samples were collected by the manufacturer at ambient temperature at the plant on 5-13-83 in 30 gallon plastic drums and shipped at ambient temperature to RTI via motor freight. The samples were received at RTI on 5-24-83 and maintained at 4°C from the time of receipt through the conclusion of the study. Evaluation was carried out on the sample collected after the carbon unit (Sample pt. 2 on Fig. 1).

Preliminary treatability studies by the manufacturer have shown that a 40:1 molar excess of hypochlorite over bentazon was necessary at 24°C and pH 6.0 to achieve a 95% reduction in bentazon level. This large HOCl excess was required at both acid and alkaline pH. Since hypochlorite is not selective in its action, wastewater containing other amine bodies will consume additional reagent and will necessitate the use of an even large hypochlorite excess (90:1). Note that the desired conversion was achieved at the expense of increasing the salt content of the wastewater.

Excess hypochlorite must be destroyed before the wastestream reaches the water biotreatment facility. Sodium bisulfite has been used successfully in eliminating free chlorine although it has been shown that this reagent also regenerates bentazon from its N-chloro analog.



A technique must be developed for destroying free chlorine which will not regenerate bentazon because it interferes with the operation of the biosystem.

Free chlorine and excess bisulfite can be pollutants. Other organic materials react with hypochlorite to form products which may also be harmful. This is particularly true for amines which can form potentially toxic and explosive N-chloro compounds.[3]

The bentazon waste stream entering the activated carbon unit is expected to have the following characteristics:

pH	1.0 - 2.0
Temperature	Ambient
Bentazon Content	50 - 300 ppm

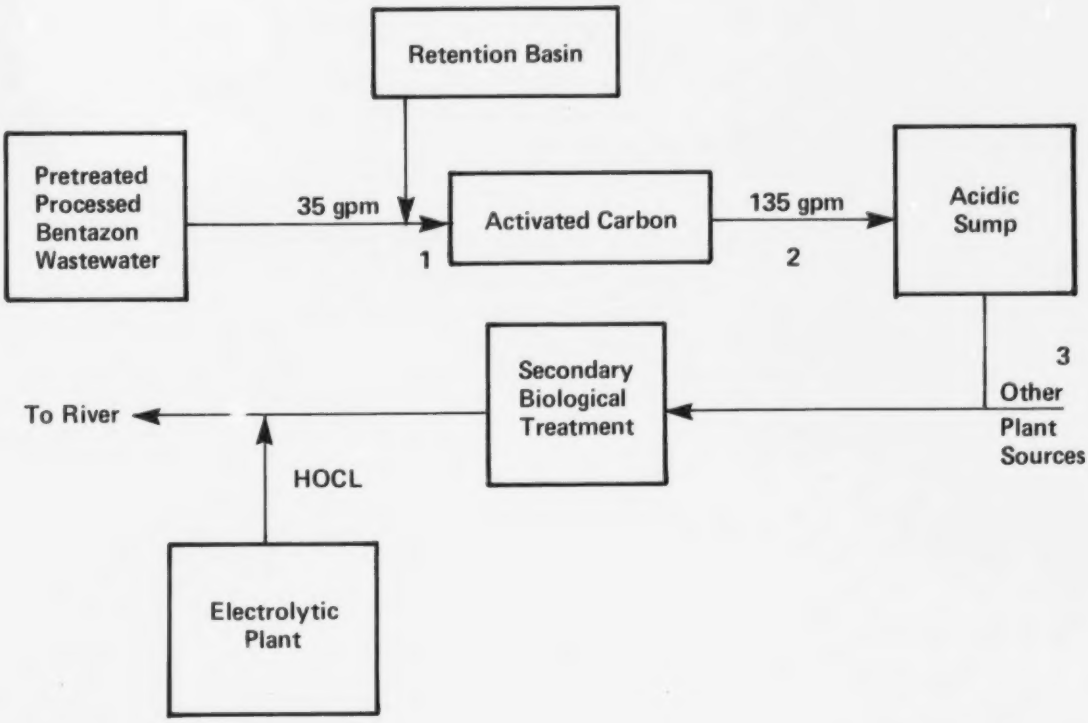


Figure 1. Wastewater treatment system.

The carbon columns step in the current treatment process removes 50-75% of the bentazon and approximately 95% of the monochlorobenzene from the wastewater. Therefore, the bentazon content of the wastewater used in this study should be between 38 and 150 ppm based on the manufacturer's information.

Treatment of Standard Bentazon Solutions with Aqueous Sodium Hypochlorite

A standard solution containing 55.2 ppm (within the 38-150 ppm range expected) bentazon was made up in one liter of Milli-Q water.* One hundred mL portions of this solution were used for preliminary experiments. Initially, a 200-fold excess of hypochlorite (2 moles hypochlorite to 1 mole bentazon) was utilized, timed aliquots of 10 mL were "quenched" in sodium bisulfite (bisulfite) to neutralize excess hypochlorite, and the bentazon determined by HPLC. Procedures for hypochlorite addition are found in Appendix A. The following five separate experiments were performed:

(1) Reagent blank (100 mL Milli-Q water). Treated directly with hypochlorite.

(2) Dilution blank. Bentazon solution with water in place of hypochlorite and bisulfite.

(3) Neutral pH. Bentazon solution treated directly with hypochlorite.

(4) Acidic pH. Bentazon solution adjusted to pH 4 with HCl before addition of hypochlorite.

(5) Basic pH. Bentazon solution adjusted to pH 10 with NaOH before addition of hypochlorite.

The results were expressed as % bentazon remaining. The response of the HPLC (Appendix B) to bentazon was linear over the range 2.5-50 ppm, so comparison to the diluted standard gave accurate recoveries. Results of the analysis of aliquots removed over time are found in Figure 2.

In all cases, the bentazon disappeared very quickly but was "regenerated" after a period of time, slowly disappearing again from solution. This suggests that a rapid reversible reaction occurs which slowly equilibrates followed by the less rapid formation of the final treatment product. The disappearance of bentazon was more rapid from neutral and acid solutions.

In a subsequent experiment, a 100 mL portion of standard bentazon solution was treated with a 333-fold excess of hypochlorite, aliquots were removed over time and analyzed. No bentazon was found in any of the aliquots (just after hypochlorite addition up to 1 hr later).

Treatment of Bentazon-Containing Wastewater

Aliquots of wastewater taken after the carbon unit were treated as described below.

* Millipore brand reagent grade water (18 megohm Resistivity at 25°C)

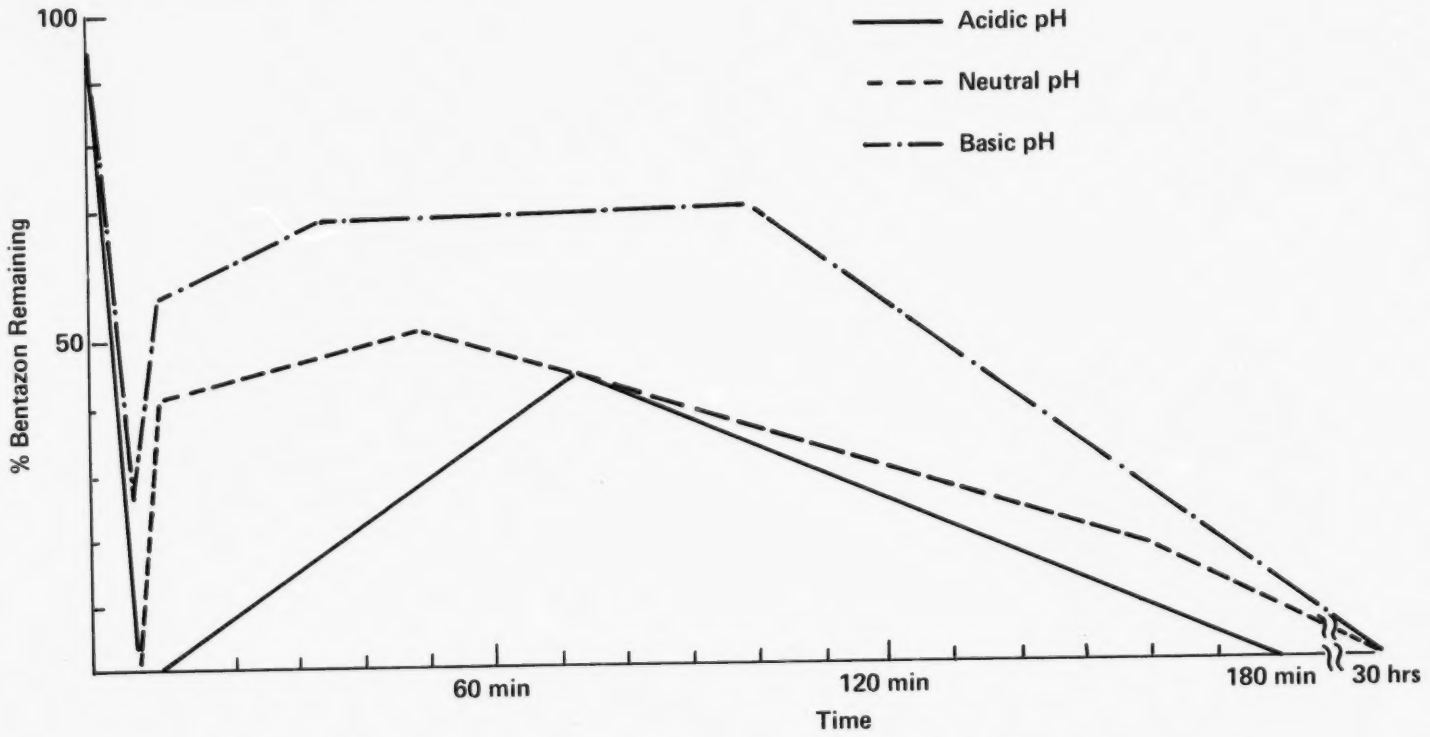


Figure 2. Treatment of standard bentazon solutions with 200-fold hypochlorite excess.

A. Hypochlorite:333-fold excess

Exp. No.	pH
BG-10	1
BG-19	2
BG-16	3
BG-17	4
BG-3	6

B. pH ≅1.5

	Exp. No.		
Temp.	20-28°C	3-7°C	Excess Hypochlorite/Bentazon
	BG-2,10	BG-20	333:1
	BG-11		167:1
	BG-12	BG-21	83:1
	BG-13		17:1

333-Fold Excess Hypochlorite at pH 1 & pH 6

Timed aliquots were taken after the addition of hypochlorite to 100 mL portions of the wastewater and quenched in a slight excess of bisulfite. A second aliquot was taken immediately and quenched in 3 fold amount of bisulfite to test the effect of excess bisulfite on bentazon concentration. Dilution blanks at pH 1 and pH 6 were also run. Results of HPLC analysis of the timed aliquots are found in Figure 3.

From Figure 3, it can be seen that with the use of a 333-fold excess of hypochlorite at pH 1, the bentazon disappeared almost completely within 10 minutes. The amount of bisulfite excess made little difference in the amount of bentazon detected. At pH 6, the bentazon disappeared more slowly and even after 60 minutes more than 55% remained. Some of the samples were not analyzed on the day the experiment was run but at a later date. The values obtained by HPLC were higher by about 25% for these samples. However, in a later re-analysis of the pH 1.5 samples, all remained at zero or low values. It is possible that the large amount of flocculent material present in the quenched aliquots may interfere in the analysis, or that some bentazon is regenerated upon standing under certain conditions.

333-Fold Hypochlorite Excess at pH 2, 3, and 4

Timed aliquots were taken from each of 3-100 mL portions of wastewater adjusted to pH 2, 3, and 4 with 10N NaOH and then reacted with a 333-fold excess of hypochlorite. All aliquots were analyzed by HPLC after quenching with bisulfite. The results are shown in Figure 4. The reaction at pH 2 was nearly identical to the reaction at pH 1.5; i.e., bentazon disappeared immediately and was only observed in very small amounts or not at all up to 3 hrs. The reaction at pH 4 was more similar to the previous reaction carried out at pH 6. Some bentazon disappeared early in the reaction (10 min) but approximately 70% remained even after 3 hrs. The pH 3 reaction showed the bentazon concentration dropping off rapidly at first and then

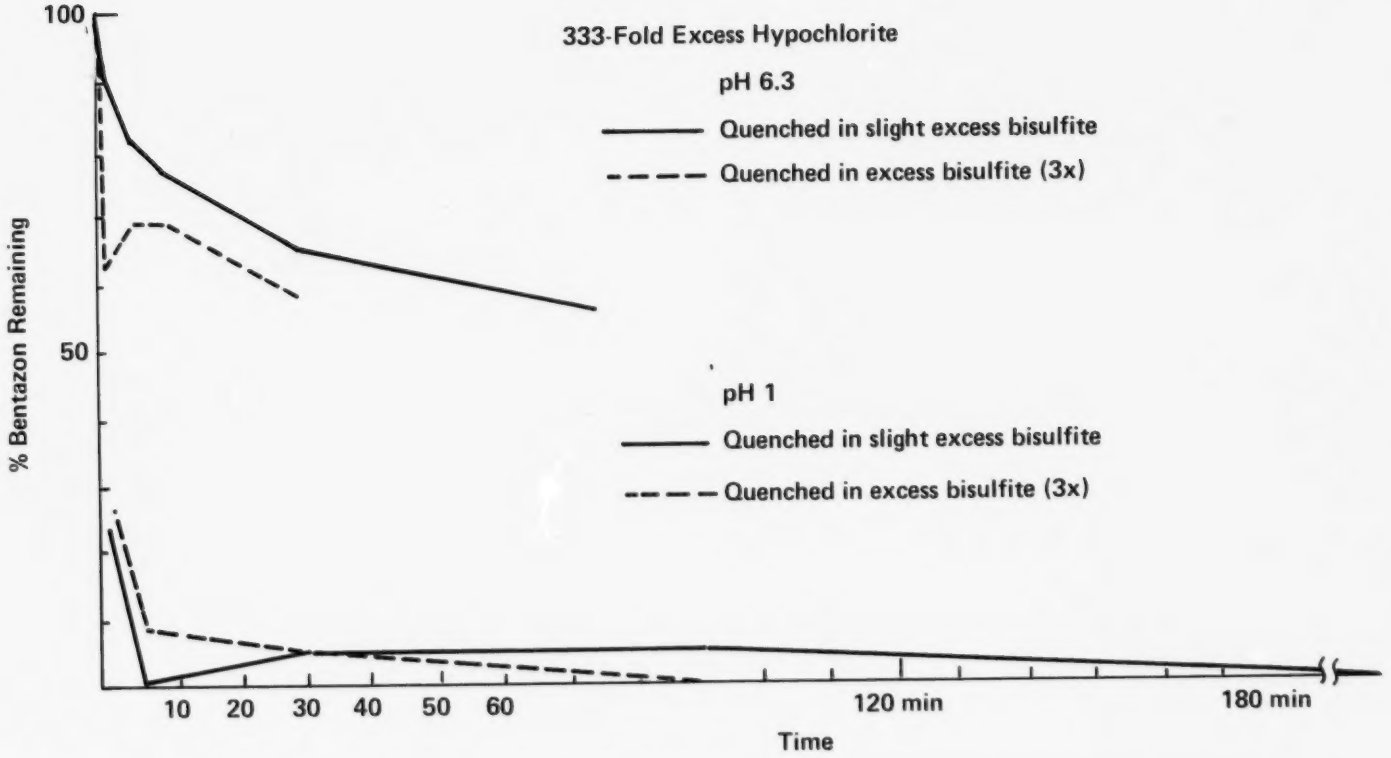


Figure 3. Bentazon-containing wastewater treated with excess hypochlorite at pH 1 and pH 6 and quenched in slight and 3-fold excess of bisulfite.

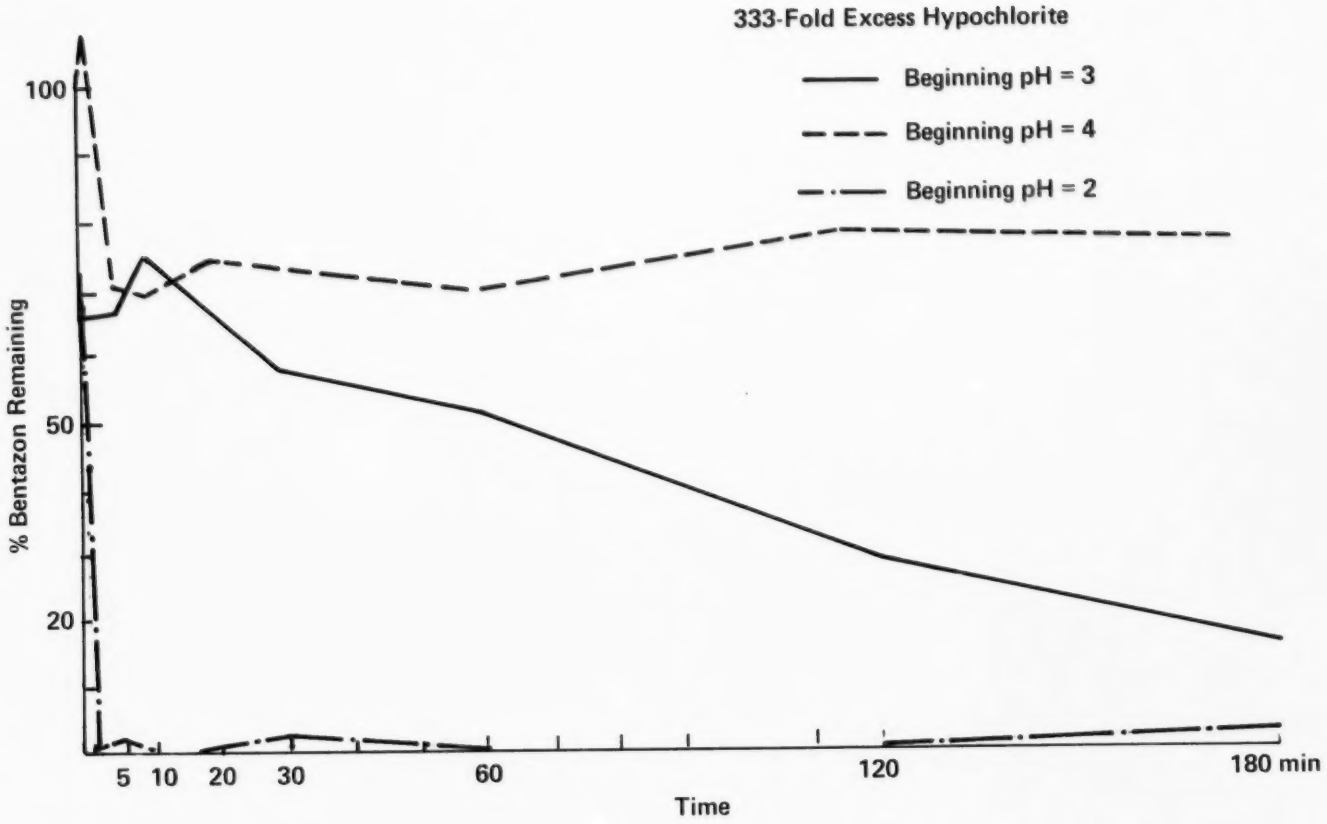


Figure 4. Bentazon-containing wastewater treated with hypochlorite at pH 2, pH 3, and pH 4.

decreasing at a much slower rate to a concentration of about 20% after 3 hrs. Another aliquot was taken at 5 hrs and the bentazon concentration was still about 19%.

There was a distinct change in the reaction between pH 2 and pH 3. The mechanisms involved in this treatment are not known. The reaction mixture has been titrated at the end of 3 hours and still contained excess hypochlorite. The physical appearance and amount of insoluble material varied with time and conditions.

Variations of Temperature and Hypochlorite Added to Wastewater

Figure 5 shows the results of 2 experiments: in the first, 100 mL aliquots were treated with a 333-fold excess of hypochlorite at room temperature and near 0°C; and in the other, 100 mL aliquots were treated with a 83-fold excess of hypochlorite at room temperature and near 0°C. When a 333-fold excess of hypochlorite was added, the bentazon disappeared rapidly and was essentially gone in 5 to 10 minutes. When this reaction was carried out at near zero (3-7°C), the reaction proceeded at a slower rate but resulted in the nearly complete removal of bentazon. This indicates that bentazon removal could be accomplished at winter temperatures as low as the freezing point.

The low temperature reaction using an 83-fold excess of hypochlorite proceded much more slowly than the ambient reaction. In fact, at all points studied, more bentazon was detected than was originally present. The effect of excess hypochlorite is further illustrated in Figure 6. The bentazon remaining in the reaction mixture is plotted against time for trials using a 167-, 83-, and a 17-fold hypochlorite excess at room temperature. Notice that the scale is now 0-1000% bentazon remaining and not 0-100% as before. The early appearance of what appears to be additional bentazon in experiments using less than 333:1 addition of hypochlorite is striking. There is no explanation for this phenomenon.

Stepwise Addition of Hypochlorite to Bentazon-Containing Wastewater

Several additional experiments were performed to determine more about the nature of the hypochlorite-bentazon reaction. First, half the amount necessary for complete reaction was added (167-fold excess), and the reaction followed for 30 minutes. Another 167-fold hypochlorite excess was added and the reaction followed for another 30 minutes. Results are shown in Figure 7. The same behavior was observed as before -- the 167-fold excess of hypochlorite resulted in an apparent 300% increase in bentazon by HPLC. However, the second 167-fold addition caused the reaction to behave as if a 333-fold excess had been added originally; that is, the bentazon disappeared almost completely within a few minutes.

In another experiment, hypochlorite was added to the bentazon-containing wastewater in increments every 5 minutes. Aliquots were taken before each new hypochlorite addition. Figure 8 shows the bentazon remaining in the reaction mixture as a function of the step-wise addition of hypochlorite. The bentazon increased as expected with each addition until a critical point was reached, then rapidly, fell off. This point was between 245 and 370 equivalents of hypochlorite. Interestingly, the characteristic purple color of this experiment did not disappear until after the bentazon was gone.

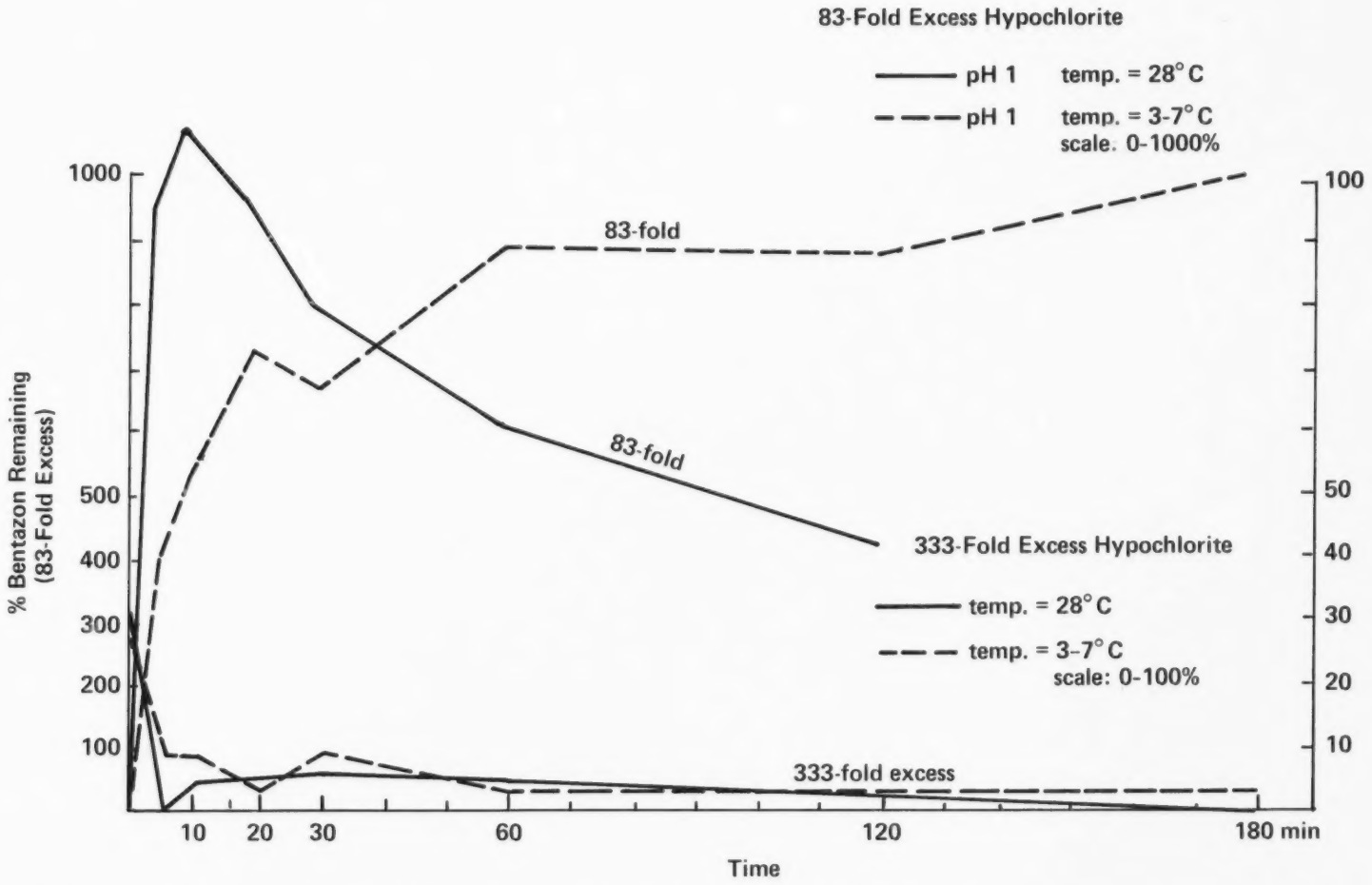


Figure 5. Effect of temperature on the disappearance of bentazon in the presence of hypochlorite.

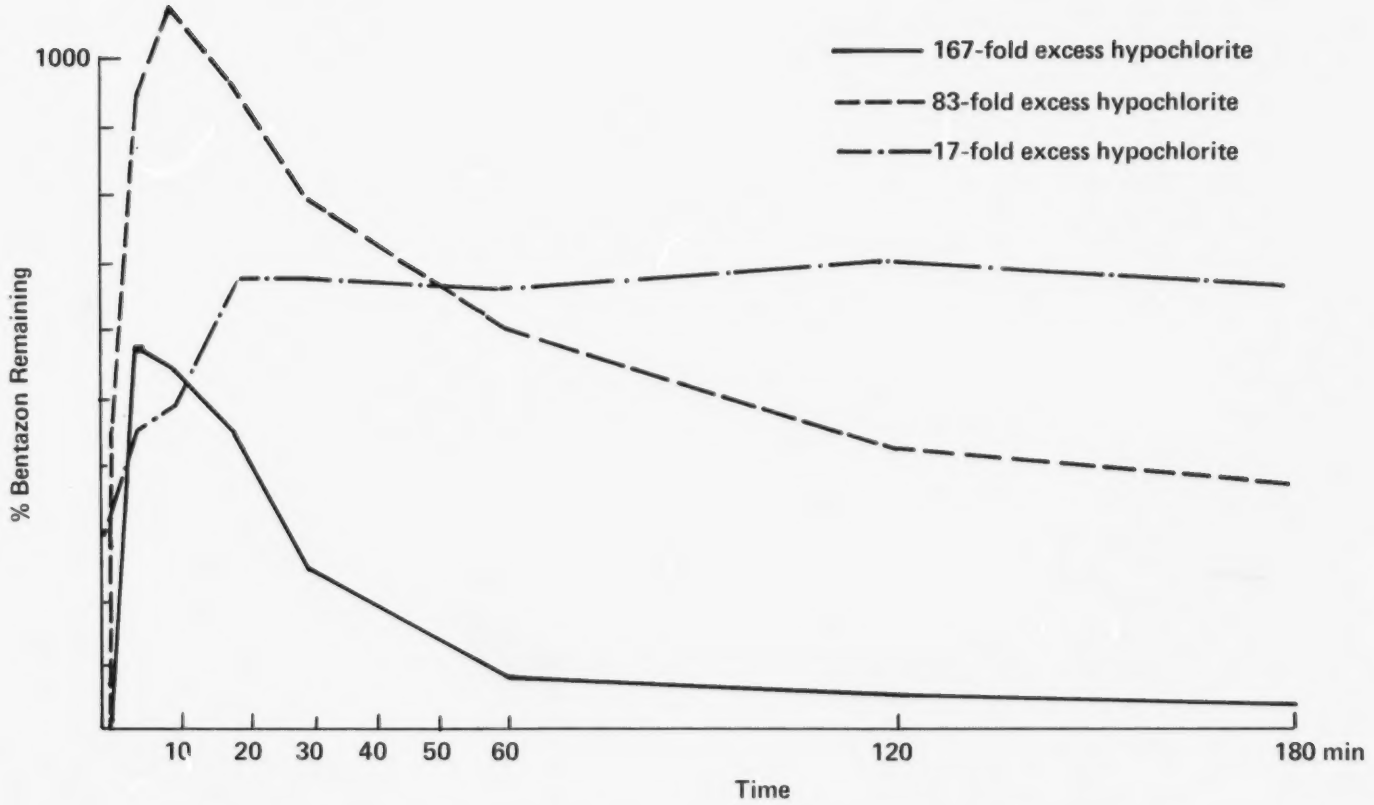


Figure 6. Addition of various amounts of hypochlorite to bentazon-containing wastewater.

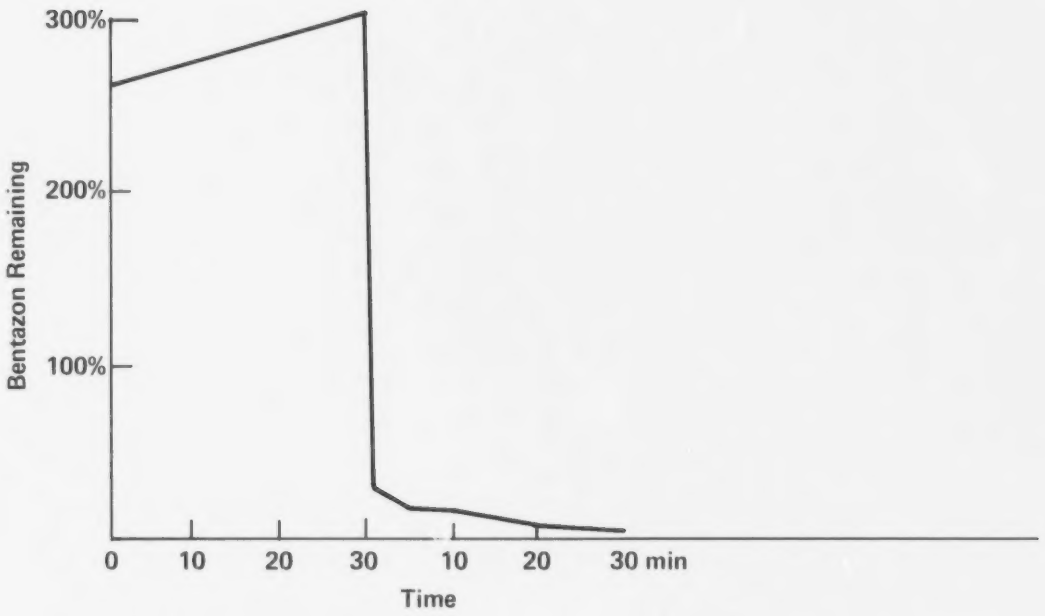


Figure 7. Addition of 167-fold excess hypochlorite to bentazon-containing wastewater initially and after 30-minute interval.

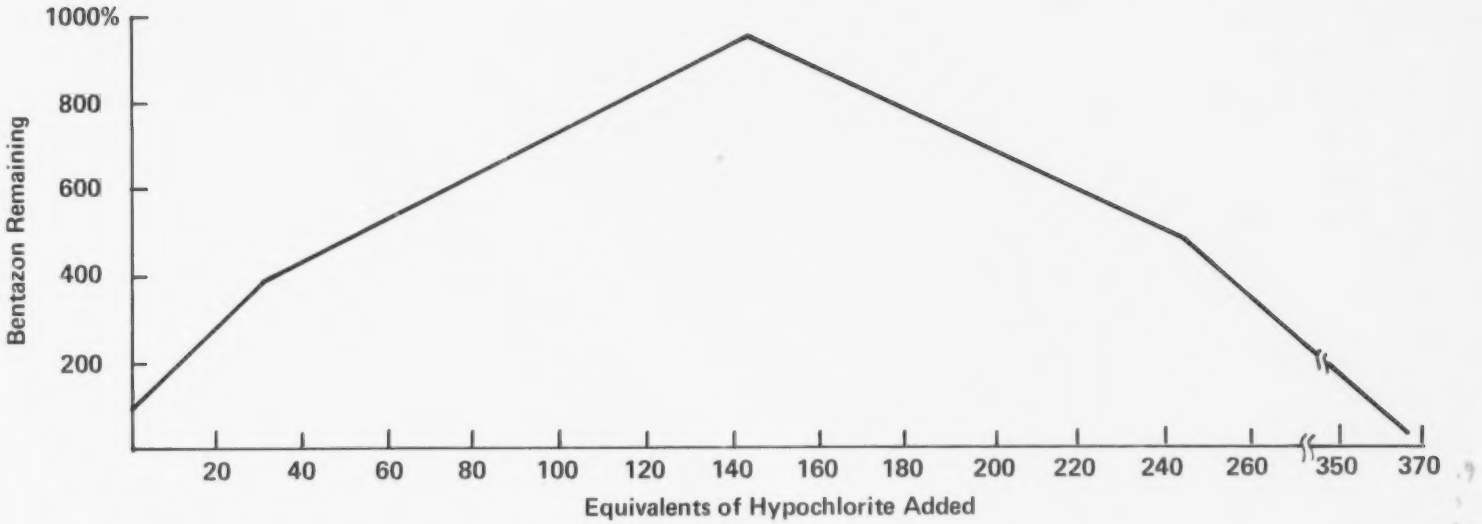


Figure 8. Stepwise addition of hypochlorite to bentazon-containing wastewater.

Fine-Tuning of Hypochlorite Addition to Bentazon-Containing Wastewater

In order to determine more precisely the amount of hypochlorite needed to remove bentazon from the wastewater in a reasonable amount of time (10-30 min.), several concentrations were investigated between 167- and 333-fold excess hypochlorite: 200-fold excess hypochlorite to correspond to 200-fold excess studied on standard bentazon and 266-fold excess (20% less than 333- fold excess). An experiment was also carried out using a 500-fold excess (50% greater than 333-fold excess). The experiments were carried out just as previous experiments, timed aliquots were taken, quenched with bisulfite and analyzed by HPLC. The results of these experiments are shown in Figure 9.

It can be seen that neither the 200-fold or 266-fold excess hypochlorite was as effective as the 333-fold excess in removing bentazon from wastewater. The 500-fold excess was, however, quite effective in removing 98% of the Bentazon in a 5 minute reaction time.

The timed aliquots were analyzed by HPLC and also qualitatively by Thin Layer Chromatography (TLC). At the end of the experiment, a portion of the reaction mixture was extracted with methylene chloride and the extract analyzed by TLC. Dichlorobentazon was seen in all three reaction mixtures, the largest amount in the experiment using 266- fold excess hypochlorite. This reaction also contained the largest variety of compounds seen by TLC.

Scaled-Up Treatment of Bentazon Containing Wastewater with Hypochlorite

Using the most favorable conditions from previous experiments (low pH with addition of 333-fold excess hypochlorite), the reaction was scaled up to 1 liter of wastewater. An aliquot was taken before addition of hypochlorite, immediately after hypochlorite addition, and again after 10 and 30 minutes. The entire reaction mixture was then quenched with bisulfite. A final aliquot was taken 10 minutes after bisulfite addition. The results are found in Table 1. The removal of bentazon from solution was essentially the same as the corresponding 100 mL reaction.

Identification of Dichlorobentazon as Reaction Product of Hypochlorite with Bentazon

The major product of hypochlorite with bentazon was initially assumed to be dichlorobentazon based on TLC studies of the reaction. In order to positively identify it as the reaction product, authentic bentazon was treated with hypochlorite, and the product isolated and characterized.

Preliminary experiments with authentic bentazon showed that under acidic conditions dichlorobentazon was seen 10 minutes to 162 minutes after hypochlorite addition. Bentazon was extractable with methylene chloride from neutral and acidic, but not basic solutions. After testing on a small-size reaction, the following procedure was used to isolate dichlorobentazon:

a. Prepare 55.2 ppm solution bentazon made acidic (pH 1-2) with 0.1 N HCl,

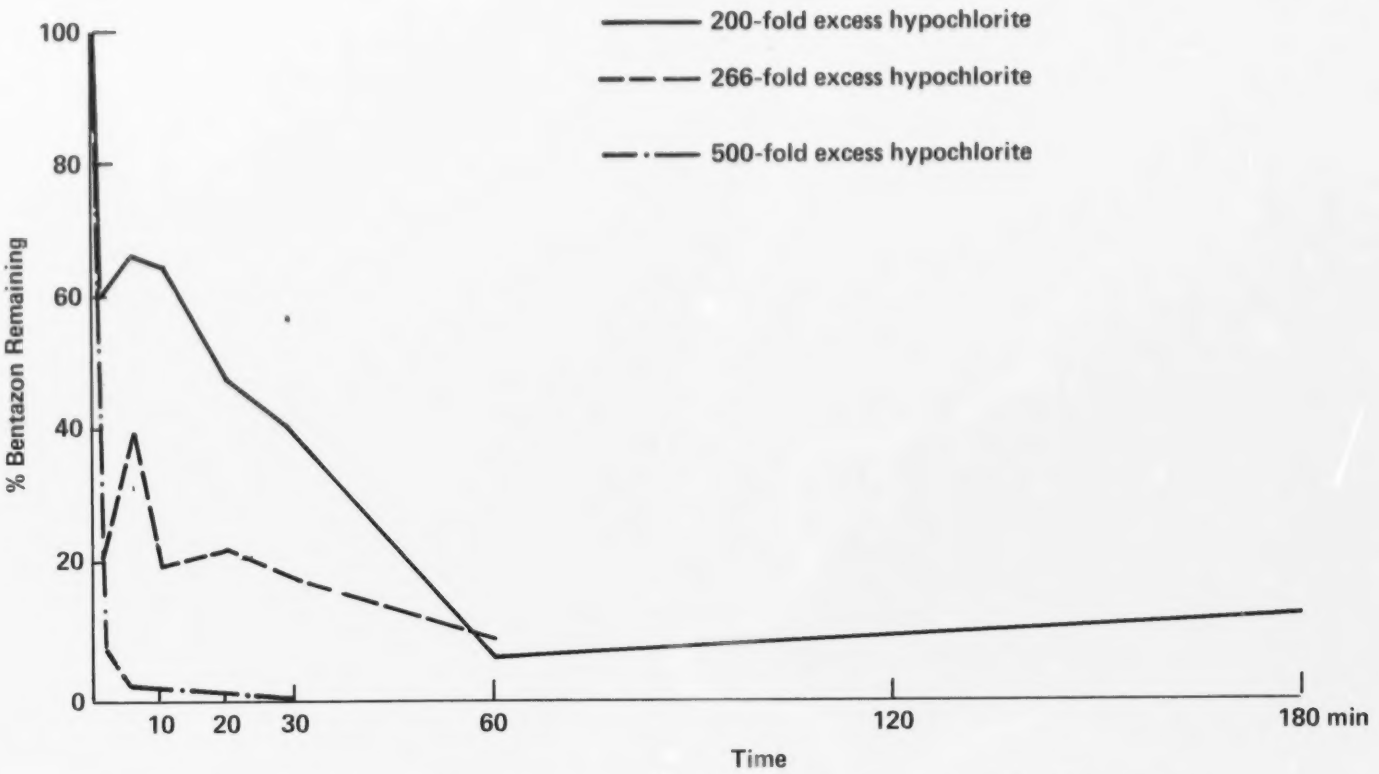


Figure 9. Addition of different hypochlorite excesses to bentazon-containing wastewater.

Table 1. LARGER SCALE TREATMENT OF BENTAZON-CONTAINING WASTEWATER WITH EXCESS HYPOCHLORITE

Bentazon	Time	Bentazon Remaining	Temperature	Reaction
Add hypochlorite	0	100%	25°C	
	1 min	23%	27 to 29.5°C	Color changes
	10 min	1.3%		Orange, flocculant material
	30 min	-	30°C	Reddish material separates out
Add bisulfite	30 min	-	31°C	Oil globules adhere to flask walls
	40 min	-	32°C	

b. Add 200-fold excess hypochlorite,
c. After 30 minutes, add slight excess bisulfite,
d. Extract twice with methylene chloride.

Infrared spectra were generated for bentazon, dichlorobentazon and isolated product using the Nicholet FT-IR. The lack of resolution in the spectrum of the product, and the complexity and similarity of bentazon and dichlorobentazon spectra made identification impossible. The spectra are included as Figures 10 thru 12.

The same materials were subjected to low and high resolution mass spectrometry. The major treatment product was shown to be the aromatic substituted dichloro analog of bentazon. The spectrum so generated was compared to the spectrum of dichlorobentazone standard (supplied by BASF Wyandotte). A common fragmentation pattern was observed: m/e 308 (molecular ion), 264, 229, and 187. Peak-matching the 308 signal from the treated bentazon spectrum gave a mass of 307.9787, best match $C_{10}H_{10}N_2O_3SCl_2$ - empirical formula of dichlorobentazon. Thin layer chromatography and infrared spectrometric analysis of the HOCl-treated extract confirmed this structure assignment.

The presence of a second treatment product was indicated. This material gave rise to a mass signal at 282 (281.9303 - $C_{12}H_4SO_2Cl_2$). The absence of a nitrogen atom suggested the possibility that this specie may be a fragment ion.

Characterization of other compounds was not undertaken.

Daphnia Bioassay

Solutions of bentazon and dichlorobentazon were subjected to toxicity testing with Daphnia magna. The test procedure used is described in Appendix C. Acute static bioassays have been decribed by EPA[4]. The results are shown in Table 2. It can be seen that bentazon was not toxic at the levels studied: 50 ppm, 5 ppm and 0.5 ppm. The dichlorobentazon showed toxicity at all levels, and was quite toxic at 50 ppm.

Cost Estimate

A cost estimate has been prepared for the HOCl treatment of bentazon wastewater and is shown in Table 3.

The following assumptions were used in the costing preparation:

(1) 333-Fold excess of HOCl (2 HOCl/1 bentazon)
(2) 100 ppm bentazon in wastewater
(3) 30 minute residue time
(4) Use of $NaHSO_3$ to neutralize half of added HOCl
(5) Operate 270 days/year

This estimate does not take into consideration BASF Wyandotte's comment that heat exchangers would be needed that would add one million dollars to the capital costs. Installation of a storage tank for hypochlorite in

Louisiana would require heat exchangers to cool the hypochlorite to prevent decomposition. Because of the corrosivity of the hypochlorite, these exchangers must be made of carbon steel shell with titanium tubes.

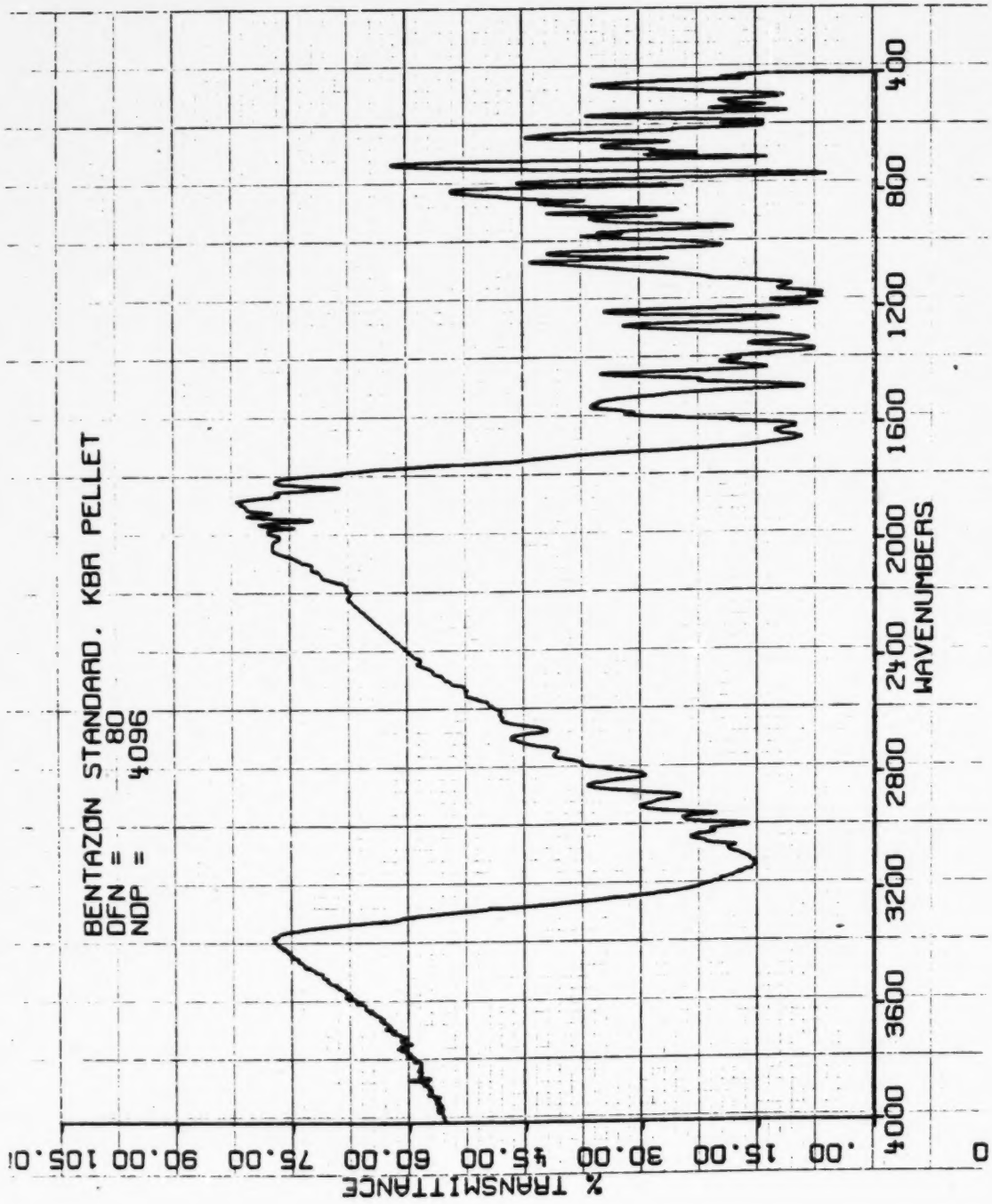


Figure 10. FT-IR Spectrum of Bentazon.

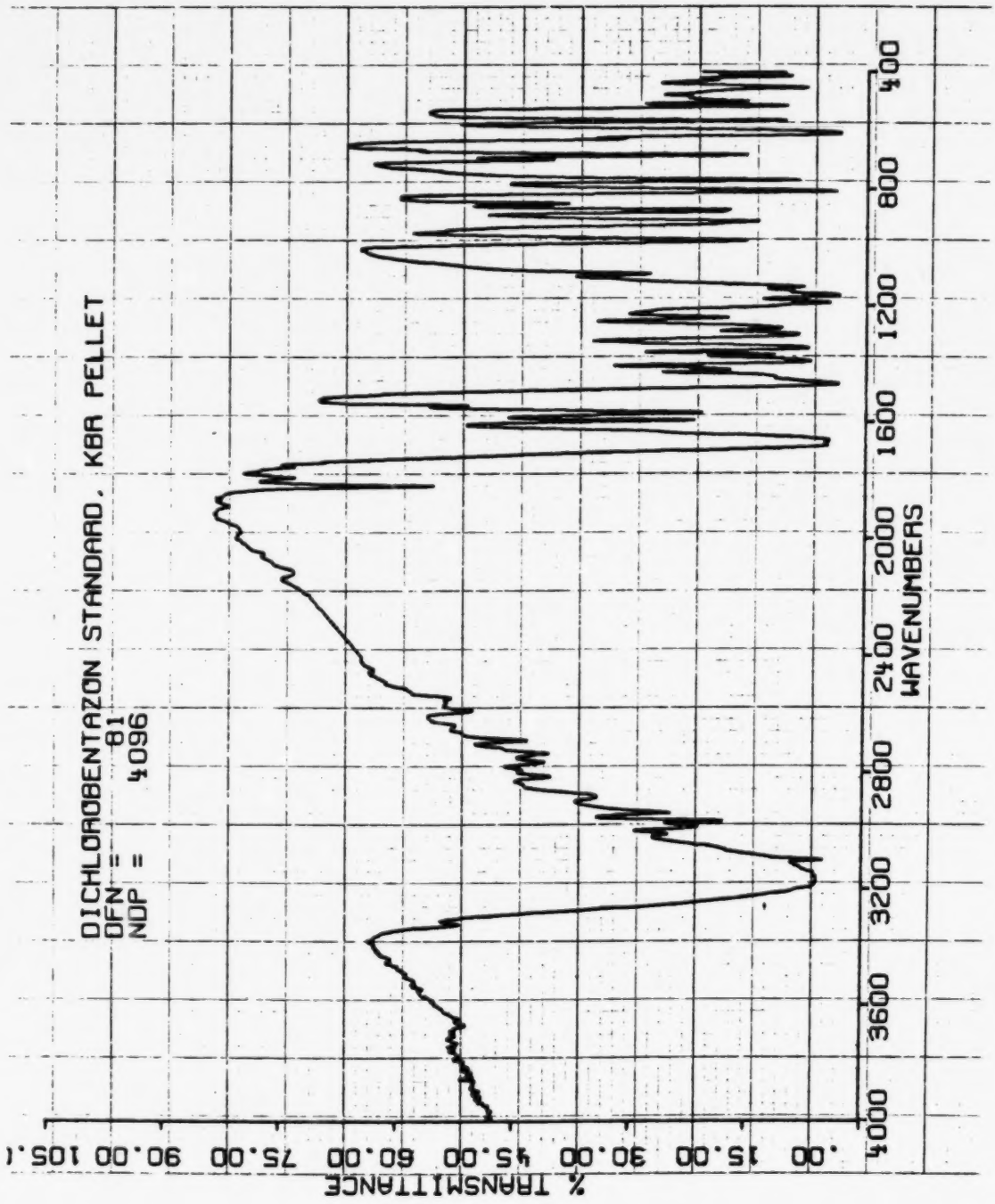


Figure 11. FT-IR Spectrum of Dichlorobentazon.

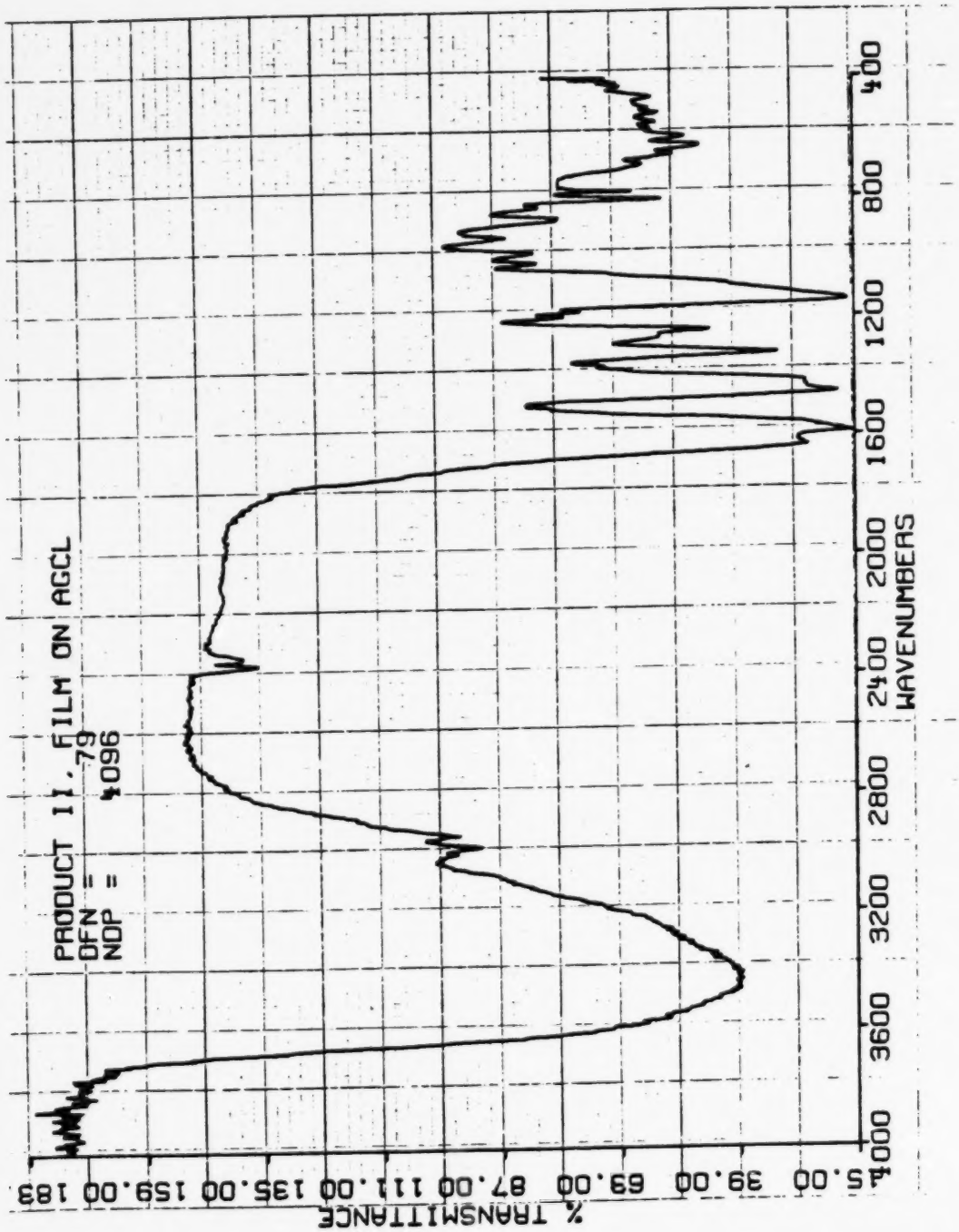


Figure 12. FT-IR Spectrum of Isolated Product.

Temperature: 27.0 - 29.5°C

Table 2. DAPHNIA BIOASSAY

Concentration, ppm	% Survivors				Conductance, μMHOS	pH
	50	5	0.5	0.0		
Bentazon - 24 hr	100	80	100	100	200 - 230	7.7 - 7.9
- 48 hr	100	80	100	100	230 - 295	
Dichlorobentazon - 24 hr	20	80	80	100	220 - 240	7.7 - 7.9
- 48 hr	0	60	40	100	200 - 245	

Table 3. BENTAZON WASTEWATER TREATMENT COST ESTIMATE (June 1983)

		Note
EQUIPMENT ITEMS:		
Hypochlorite Addition Tank	$ 12,100	A
Hypochlorite Agitator	12,300	B
Hypochlorite Feed System (Inc. Storage)	444,600	C
Bisulfite Addition Tank	5,300	D
Busulfite Agitator	5,000	E
Bisulfite Feed System	205,200	F
INSTALLED COST	685,000	
Piping	205,000	G
Instrumentation	34,200	H
CAPITAL EQUIPMENT COST	924,000	
Site Development	92,400	I
Electrical	46,200	J
TOTAL FACILITY COST	1,063,000	
Engineering, Legal, Administrating	213,000	K
TOTAL CAPITAL COST	1,276,000	
AMORTIZED CAPITAL	150,000	L
OPERATING COSTS ($/YR)		
Electrical (Mixers)	1,450	M
Maintenance (Mixers)	1,730	N
Maintenance (Tanks)	1,740	O
O & M Feed System (Inc. Electricity)	58,700	P
Labor	32,400	Q
NaOCl	2,154,000	R
$NaHSO_3$	1,196,000	S
TOTAL YEARLY OPERATING COST	$3,596,000	
ANNUALIZED AND UNIT COSTS PER YEAR -	$3,746,000	
PER GALLON -	$ 0.0714	

A. 135 gal/min x 30 min residence time = 4050 gal - say 5000 gal, 304 stainless, atmospheric, $8000. FOB (Jan 1982) - Ref. 1. x 1.05 delivered x 1.4 installed x 757/735 M&S Equipment Escalator

B. 1 HP/1000 gal, 5 HP required, stainless shelf and turbine with electric motor $2000\ (HP)^{0.56} = 200(s)^{0.56}$ = $4925 installed (July 1970) - Ref 2 x 757/302 M&S Equipment Escalator

C. NaOCl required 660 mole/mole bentazon x 74.5/240 = 205 lb NaOCl/lb bentazon. (100 mg bentazon/L)(3.78L/gal)(135 gal/min)(1b/454000 mg)(205 lb NaOCl/lb bentazon)(60 x 24) = 33181 lb NaOCl/DAY. 15% NaOCl solution is 10.26 lb/gal or 1.54 lb NaOCl gal so 21560 gal/day required. Based on ref. 3 costs for Alum, feeders; equivalent feed system at 70 MGD plant. $195,000 installed (1972) x 757/332 M&S Escalator

Table 3 (cont'd.)

D. 135 gal/min x 5 min residence time = 675 gal, 303 stainless, atmospheric, $3500 FOB (Jan 1982) Ref. 1.
x 1.05 Delivered x 1.40 installed x 751/735 M&S Equipment escalator.

E. 1 HP stainless turbine and shaft (including motor) $2000 installed Ref 2 x 751/302 M&S equipment escalator.

F. 50% of added NaOCl to be destroyed. Added 20.49 g/L NaOCl. $NaHSO_3$ required is 20.49 x 0.5 x 104/74.5 x 110% stoichiometric = 15.73 g $NaHSO_3$/L wastewater (15.73 x 3.78 x 135 x 60 x 24)/454 = 25460 16/day required -- 6090 gal/day feed as 38% soln, 11.0 16/gal, based on Ref. 3 costs for Alum feeders. Equipment feed system at 20 MGD plant. $90,000 installed (1972) x 757/332 M&S escalator.

G. 30% Installed cost
H. 5% Installed cost
I. 10% Capital Equipment Cost
J. 5% Capital Equipment Cost
K. 20% Total Facility Cost
L. 20 years at 10%
M. 6 HP x 746 kw/HP x 24 x 270 days operation x $0.05/kwhr
N. 10% Installed cost of mixers
O. 10% Installed cost of tanks
P. Ref.3 34800 x 757/332 M&S escalator x 270/365
Q. 2 hr/shift x 3 x 270 x $20.00 (Inc. fringe)
R. 21560 gal/day x 270 day x $0.37/gal (Reserve, La - Jones Chem. Co.)
S. 25460 lb/day x 270 day x $0.174/lb (Chem. Marketing Reporter 5-30-83).

1. Hall, R. S., Chem. Eng. 4/5/82, p. 86.
2. Happel, J. and D. Jorden, Chemical Process Economics, Dekker, New York (1975).
3. U.S. EPA, Process Design Manual for Suspended Solids Removal, EPA 625/1-75-003a (1975).

SECTION 6

QUALITY ASSURANCE

Project Description

Laboratory studies were conducted on the treatability of wastewater generated from the manufacture of bentazon. The wastewater was characterized for pesticide content by high performance liquid chromatography (HPLC). Toxicity determinations on bentazon and its major treatment product dichlorobentazon were conducted with Daphnia Magna.

Emphasis was placed on the removal of bentazon from wastewater by treatment with sodium hypochlorite. The effect of variations in the pH, amount of hypochlorite, temperature, and mode of hypochlorite addition were studied.

Based on assumed rates of process wastewater production, the total cost of the treatment was estimated.

Certain process information disclosed by BASF Wyandotte during the project was considered confidential and treated as such under a Secrecy Agreement between RTI and BASF executed May 12, 1983 and amended August 1, 1983.

Project Personnel

Ms. Doris J. Smith (Research Chemist) performed the experimental work on this project under the supervision of Dr. Robert W. Handy (Principal Scientist). All laboratory data were recorded in RTI Laboratory Notebook No. 4183, pp. 1-86 during the period June 8 to August 12, 1983.

Laboratory Facilities

The experimental work was carried out in Laboratory No. 101 in the Camille Dreyfus Laboratories at RTI (Figure 13). An evaluation form for Laboratory No. 101 was completed and is included in this Report (Table 4).

Sample Collection

Dr. Handy was present during the collection of samples at the Geismar, LA facility. The bentazon process was sampled on May 13, 1983 at three locations (see Figure 14) in 30 gallon plastic drums. The drums were transported by Overnight Transportation Co., leaving Geismar, LA on May 17 and arriving at RTI on May 24, 1983. The drums arrived intact with no visible signs of damage. The temperature of the wastewater samples was approximately 20°C.

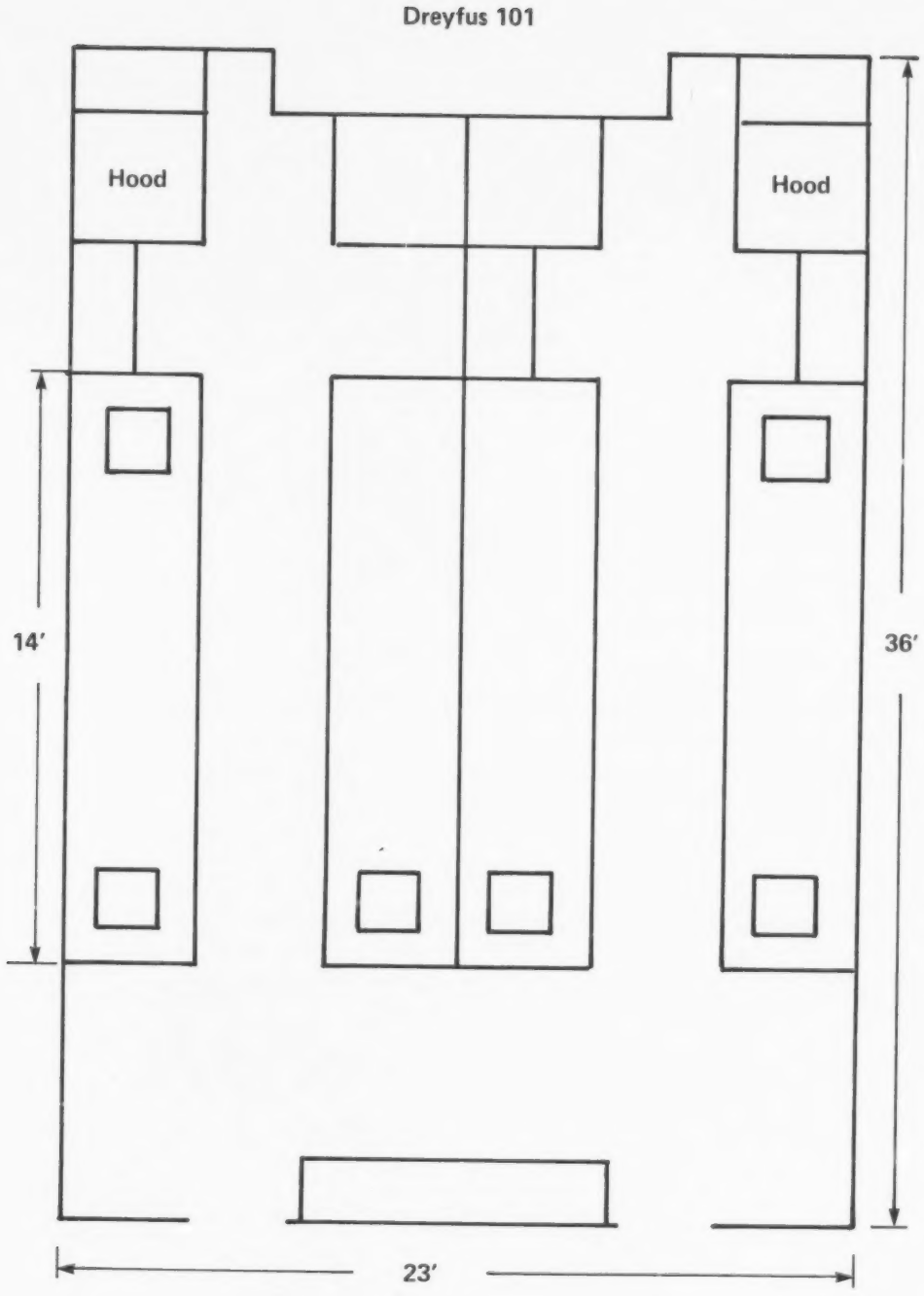


Figure 13. Dreyfus laboratory 101.

Table 4. LABORATORY EVALUATION FORM

		Yes	No	Comment:
1.	Does the laboratory appear to have adequate workspace (120 sq. feet, 6 linear feet of unencumbered bench space per analyst)?	X		See #1 below
2.	Are voltage control devices used on major instrumentation (e.g., GC/MS, spectrophotometers)?	X		On GC and HPLC
3.	Does the laboratory have a source of distilled/demineralized water?	X		From Lab 175
4.	Is the conductivity of distilled/demineralized water routinely checked and recorded?		X	
5.	Is the analytical balance located away from draft and areas subject to rapid temperature changes?	X		Analytical balance in Lab 186
6.	Has the balance been calibrated within one year?	X		
7.	Are exhaust hoods provided to allow organized work with volatile materials?			See #7 below
8.	Is the laboratory maintained in a clean and organized manner?	X		
9.	Are safe and contamination-free work areas provided for the handling of toxic or radioactive materials?	X		Toxic Lab in Bldg. 3 Fume hood in lab 101,180
10.	Are the radioactive and/or toxic chemical handling areas either a stainless steel bench or an impervious material covered with absorbent material?	X		Hood work surface covered with absorbent paper

#1. See attached sketch of Lab 101.

#7. Flow rate of air periodically checked by service technicians and recorded on chart in hood.

	Yes	No	Comment:
11. Are adequate facilities provided for storage of samples, including cold storage?	X		See #11 below
12. Are chemical waste disposal facilities adequate?	X		See #12 below
13. Are comtamination-free areas provided for trace level analytical work?	X		See #13 below
14. Can the laboratory supervisor document that trace metals-free water is available for preparation of standards and blanks?			N/A
15. Is organic-free water available for preparation of standards and blanks?	X		See #15 below
16. If biotesting is to be conducted, are adequate environment-controlled facilities available (e.g., light, temperature control)?			N/A
17. Is the required field instrumentation and sampling equipment properly maintained?			N/A
18. Is adequate safety equipment (fire extinguishers, showers, eyewash stations) located throughout the laboratory?	X		See #18 below

#11. Samples for GC and HPLC analysis stored in cold room.

#12. Jug for toxic wastes is stored in hood and emptied periodically by RTI safety personnel.

#13. No special area set-aside: lab benches and fume hoods.

#15. From Lab 175 (see #3); Purity checked approximately monthly with HPLC by various technicians-not routinely checked.

#18. Fire extinguisher in lab; Shower in hall outside lab; Eye wash station on lab bench.

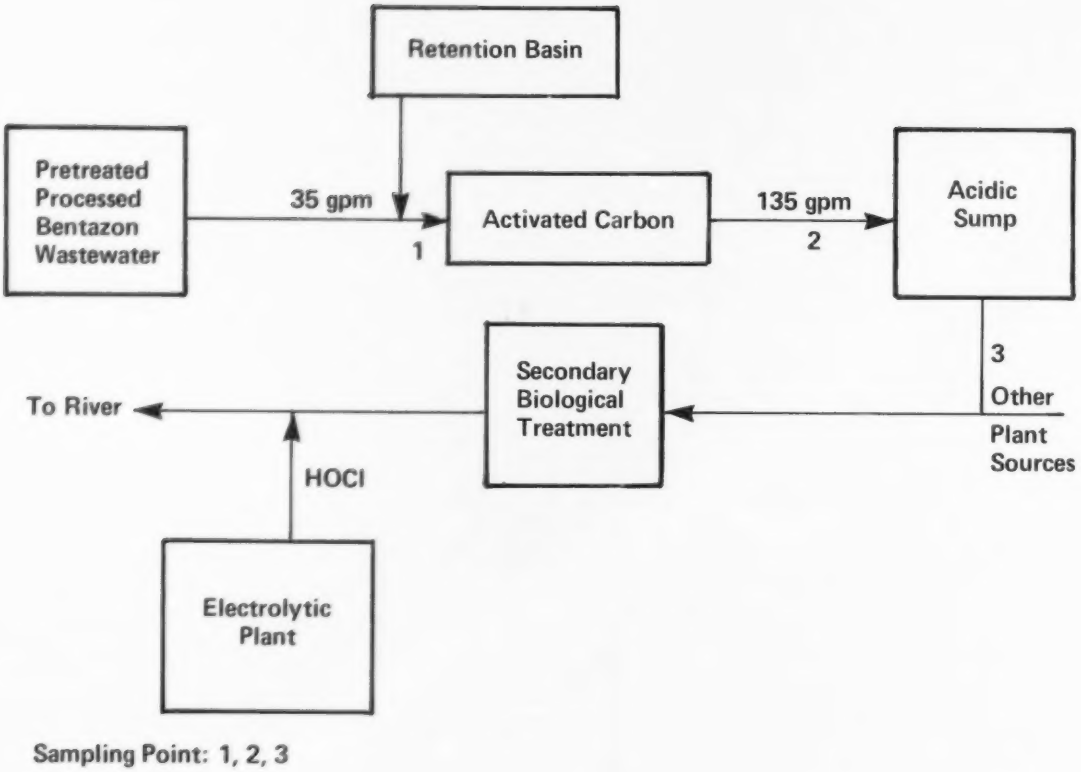


Figure 14. Sampling locations in wastewater treatment system.

General Treatment Procedure

The basic treatment operation involved four main steps: pH adjustment, hypochlorite addition, quench ($NaHSO_3$) treated aliquot, and HPLC analysis. This scheme is shown in Figure 15. All of the treatment experiments were carried out with wastewater collected at location 2 (Figure 14).

Analytical Methodology

High Pressure Liquid Chromatography (HPLC) conditions were the same or very similar to those outlined in BASF Wyandotte Standard Technical Instructions No. 8507-283:

(1) High performance solvent delivery system, Waters Assoc. M6000 pump

(2) UV Detector operating at 340 nm, Schoeffel Model 770

(3) Radial Compression Module and a 10 micron C_{18} Radial Pak Column from Waters

(4) Solvent System 65:35 pH 6 sodium acetate buffer:MeOH

(5) Solvent flow, 2.0 ml/min; Injection volume, 10 µL

The HPLC system worked well with bentazon eluting 3.2 minutes after injection. Repetitive 10 µL injections of 5 ppm standard showed a C.V. of 5.5% (n=8); 10 µL injections of 25 ppm standards, a C.V. of 2.1% (n=6). The working detection limit was 1 ppm with lower levels easily attainable. A study to determine interlaboratory precision was not performed.

Analytical Quality Control

Standards of bentazon (obtained from BASF Wyandotte) were prepared in Milli-Q water for HPLC analysis at 2.5, 5, 25, and 50 µg/mL. Each was weighed and prepared independently. At the beginning of each analysis day, one 10 µL injection of each standard was made. The linear regression calibration was calculated and judged to be acceptable before sample injections were begun. Standards were injected after each 4 - 6 samples to be sure the calibration was stable.

A method blank was prepared by adding all experimental reagents to a 100-mL aliquot of Milli-Q water. The blank was treated in the same manner as a bentazon-containing sample.

Dilution blanks were also run on a solution of 55.2 ppm bentazon (standard from BASF Wyandotte) prepared in Milli-Q water. Distilled water was added to each of three 100-mL aliquots (one at approximately pH 7, one made to pH 4 with HCl, and one to pH 9 with NaOH) instead of the experimental reagents. All experiments carried out on the prepared 55.2 ppm solution were quantitated against the dilution blank and checked using the calibration "curve".

Similarly, dilution blanks were prepared for the bentazon wastewater by adding water instead of reagents to 100-mL aliquots at neutral, acidic, and

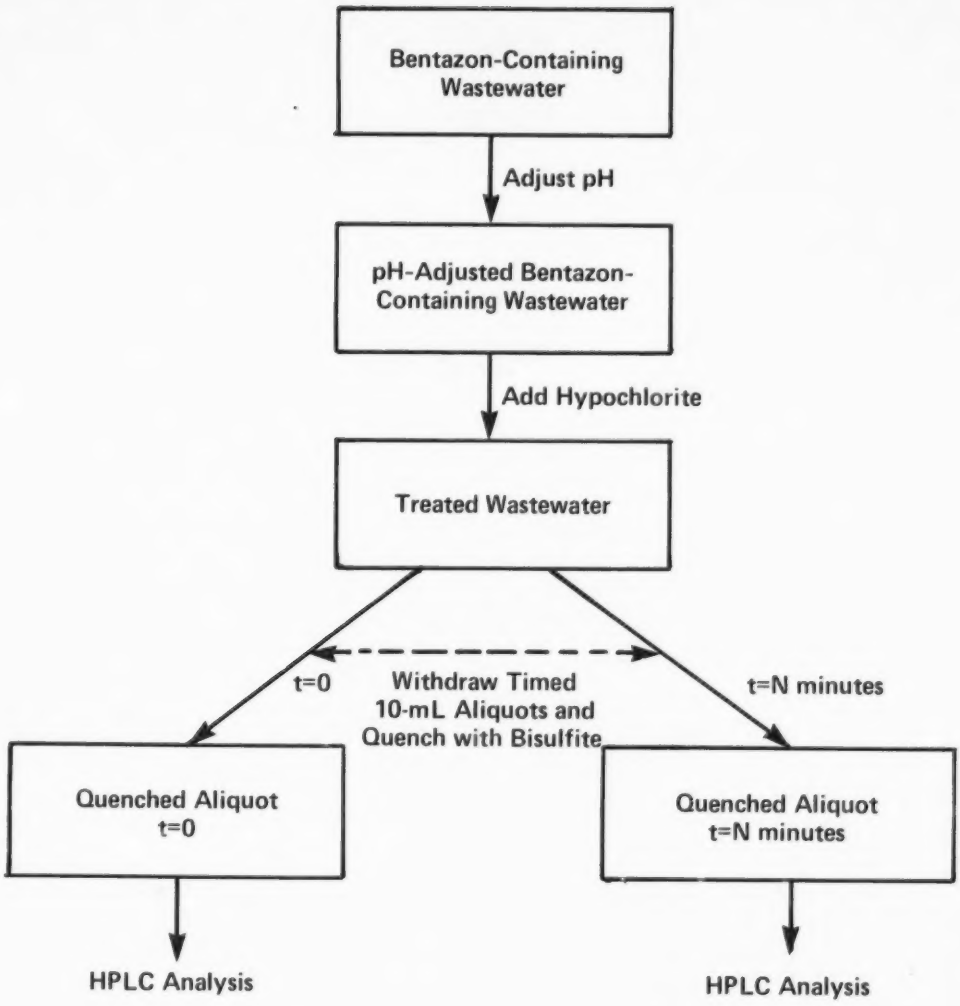


Figure 15. Flowsheet of wastewater treatment procedure.

basic pH. These dilution blanks were prepared at the beginning of the experiments and run each day on the HPLC. Another set of dilution blanks was prepared near the end of the set of experiments to be sure no changes had occurred in the blanks. The percent bentazon remaining in an experimental aliquot was determined using the dilution blank and checked with the daily calibration curve.

REFERENCES

1. Sittig, M. Pesticide Manufacturing and Toxic Materials Control Encyclopedia. Noyes Data Corp., Park Ridge, NJ, 1980.

2. Gaynor-Weed Society of America "Herbicide Handbook of the Weed Science Society of America", Weed Science Society of Ameria; Champaign, IL, 1974.

3. Private communication, BASF Wyandotte.

4. Duke, K.M., Davis, M.E. and Dennis, A.J., IERL-RTP Procedures Manual: Level 1 Environmental Assessment Biological Tests for Pilot Studies. EPA-600/7-77-043.

APPENDIX A

PROCEDURES PROTOCOL FOR HYPOCHLORITE ADDITION TO WASTEWATER WITH SUBSEQUENT TREATMENT WITH BISULFITE

Commercial 5.2% aqueous sodium hypochlorite was used for hypochlorite additions. The particular batch of hypochlorite used in these experiments was titrated with thiosulfate to determine available chlorine according to Standard Methods for the Examination of Water and Wastewater, 15th Edition (APWA, AWWA, WPCF, 1980) using Method 409A. The determination was 5.05% hypochlorite and this value (50.5 g/L) was used to calculate the amount needed for addition to the wastewater.

Since the end product of bentazon chlorination is predominantly dichlorobentazon, stoichiometry was assumed to be 2 moles of hypochlorite: 1 mole bentazon. Therefore, a 333-fold excess of hypochlorite would be 666 moles of hypochlorite: 1 mole bentazon.

All reactions (unless otherwise stated) were carried out in beakers in a fume hood at room temperature. At time zero, all the hypochlorite was added to 100 mL wastewater (using a pipet or repipet), stirred briefly, and the first aliquot withdrawn and quenched with bisulfite. Bisulfite was premeasured into a scintillation vial and the aliquot added to it. Aqueous sodium bisulfite (10 g/100 ml) was used for quenching. 1.1 mole of bisulfite per 1 mole hypochlorite was added to a 10 mL aliquot of treatment mixture.

The first aliquot was considered to be at time zero, although the aliquot was taken at some finite time after addition of hypochlorite. The quenched samples were analyzed by HPLC as quickly as possible, in most cases within an hour or two after being removed.

The low temperature experiments were done in Ehrlenmeyer flasks in an ice bath with magnetic stirring.

APPENDIX B

ANALYTICAL PROCEDURES FOR BENTAZON

HPLC

HPLC conditions were the same or very similar to those outlined in BASF Wyandotte Standard Technical Instructions No. 8507-283:

High performance solvent delivery system, Waters Assoc. M6000 pump

UV Detector operating at 340 nm, Schoeffel Model 770

Radial Compression Module and a 10 micron C_{18} Radial Pak Column from Waters

Solvent System 65:35 pH 6 sodium acetate buffer:MeOH

Solvent flow, 2.0 ml/min

Injection volume, 10 µL

Bentazon eluted in 3.2 minutes and the latest peak 9.2 minutes after injection. Repetitive 10 µL injections of 5 ppm standard showed a C.V. of 5.5% (n=8); 10 µL injections of 25 ppm standards, a C.V. of 2.1% (n=6). The working detection limit was 1 ppm with lower levels easily attainable with larger injection size.

TLC

Since gel layers impregnated with a fluorescent indicator were developed in one of two equivalent solvent systems recommended by BASF Wyandotte:

I. Cyclohexane/Toluene*/Dioxane/Acetic Acid 70:20:25:4

II. Toluene*/Dioxane/Acetic Acid 90:25:4

Bentazon and dichlorobentazon were identified under UV-light.
(*Toluene was substituted for benzene in BASF Wyandotte recommended TLC system).

APPENDIX C

DAPHNIA MAGNA BIOASSAY

Range-Finding Bioassay

(1) Prepare 100 mL of the following dilutions in 250 mL beakers: undiluted wastewater, 10% in hard water, 1%, 0.1%, and 0.01%. Put 100 mL of hard water in a 250 mL beaker to serve as a control.

(2) Measure the pH, conductivity, dissolved oxygen and temperature of each test solution. Adjust the pH of each solution to 8.0 ± 0.5.

(3) Add 5 daphnids to each beaker. The daphnids do not need to be less than 24 h old or even the same age.

(4) Cover each beaker with a petri-dish and place all beakers in the temperature-controlled room.

(5) After 24 h, count the survivors in each beaker.

(6) If necessary, repeat the range-finding bioassay with a more dilute range of wastewater concentrations.

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